Chemical Equilibria in Hydrolysis of Germanium Tetrachloride and Arsenic Trichloride

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Abstract—The chemical equilibria in the hydrolysis of high-purity germanium tetrachloride and arsenic trichloride at low water concentrations were studied by IR spectroscopy. The equilibrium constant of $AsCl_3$ hydrolysis was shown to correlate with the activity coefficient of $AsCl_3$. The equilibrium constants and thermodynamic characteristics of $GeCl_4$ and $AsCl_3$ hydrolysis in CCl_4 were calculated for the temperature range 283– 333 K.

INTRODUCTION

Fine purification of germanium tetrachloride and arsenic trichloride with the aim of removing oxygencontaining impurities, including hydrolysis products, is a challenging problem. The presence of dissolved water in these chlorides has a significant effect on the stability of chalcogen- and silicon-containing impurities and may lead to their transformations in the course of the purification process [1, 2].

Earlier work [3, 4] showed that, at low concentrations of dissolved water in GeCl_4 (<0.01 mol/l) and AsCl_3 (<0.04 mol/l), these chlorides hydrolyze predominantly according to the schemes

$$\operatorname{GeCl}_4 + \operatorname{H}_2 O \Longrightarrow \operatorname{Ge}(OH)\operatorname{Cl}_3 + \operatorname{HCl},$$
 (1)

$$AsCl_3 + H_2O \Longrightarrow As(OH)Cl_2 + HCl.$$
 (2)

The purpose of this work was to investigate chemical equilibria in these reaction systems.

CHEMICAL EQUILIBRIUM IN GERMANIUM TETRACHLORIDE HYDROLYSIS

The chemical equilibrium in the interaction of water $(10^{-3} \text{ to } 4 \times 10^{-2} \text{ mol/l})$ with germanium tetrachloride was studied using both high-purity GeCl₄ and mixtures of GeCl₄ and CCl₄ $(10^{-3} \text{ to } 8.74 \text{ mol/l GeCl}_4)$.

Carbon tetrachloride was used as a solvent because it is nonreactive with H_2O and $GeCl_4$ and also because the $GeCl_4$ – CCl_4 system behaves ideally and, accordingly, the CCl_4 solvent has no effect on the v(OH) frequency of $Ge(OH)Cl_3$ and the molar extinction coefficient in the maximum of this band in the spectra of pure $GeCl_4$ and its solutions in CCl_4 . Moreover, as shown earlier [5], water is in a monomeric form in CCl₄ at concentrations from 10^{-4} to 2×10^{-2} mol/l, and the v(OH) bands of H₂O (3705 cm⁻¹) and Ge(OH)Cl₃ (3603 cm⁻¹) are well resolved. Carbon tetrachloride has no absorption bands in the OH stretching region. This situation, ideal from the viewpoint of experiment, allows one to accurately determine the equilibrium constants of reaction (1) in CCl₄ by monitoring the intensity of the v_{as} band of water (3705 cm⁻¹) during hydrolysis.

The equilibrium of reaction (1) in CCl₄ was studied at 293 K with vigorous stirring, using a thermostated reactor and a flow cell made of optical quartz glass, with an absorbing layer thickness of 10 cm [6]. Highpurity GeCl₄, containing $<10^{-4}$ mol/l H₂O, was added to appropriate amounts of CCl₄ and water. The IR transmission spectrum of the solution was recorded at 293 K from 3200 to 4000 cm⁻¹ before and after the introduction of GeCl₄ (Fig. 1). As a result of hydrolysis, the intensity of the v_{as} band of water (3705 cm⁻¹) decreases, and the OH stretching band of Ge(OH)Cl₃ emerges at 3603 cm^{-1} . The approach to equilibrium in reaction (1) was followed by repeatedly recording the spectrum of the solution. The equilibrium reactant and product concentrations in reaction (1) were calculated by the relations

$$C_{\rm eq_{Ge(OH)Cl_{3}(HCl)}} = \frac{A'_{\rm H_2O} - A''_{\rm H_2O}}{\varepsilon_{\rm v_{as}(\rm H_2O)}l},$$
(3)

$$C_{\rm eq_{\rm H_2O}} = \frac{A_{\rm H_2O}^{"}}{\varepsilon_{\rm v_{ac}({\rm H_2O})}l},$$
(4)

$$C_{eq_{GeCl_4}} = C_{i_{GeCl_4}} - C_{eq_{Ge(OH)Cl_3}},$$
 (5)



Fig. 1. IR transmission spectra of (1) H₂O and (2) H₂O + GeCl₄ solutions in CCl₄; 2.44×10^{-3} mol/l H₂O, 1.6×10^{-1} mol/l GeCl₄, 10-cm absorbing layer.

where $C_{eq_{Ge(OH)Cl_3}}$, $C_{eq_{HCl}}$, $C_{eq_{GeCl_4}}$, and $C_{eq_{H_2O}}$ are the Ge(OH)Cl_3, HCl, GeCl_4, and H₂O concentrations (mol/l) in the equilibrium mixture; $C_{i_{GeCl_4}}$ is the GeCl_4 concentration in the starting mixture; A'_{H_2O} and A''_{H_2O} are the maximum absorbances on the v_{as} band of water in the spectrum of the H₂O + CCl₄ mixture and in the spectrum of the equilibrium H₂O + GeCl_4 + Ge(OH)Cl_3 + HCl + CCl_4 mixture, respectively; $\varepsilon_{v_{as}(H_2O)}$ is the molar extinction coefficient (l/(mol cm)) in the maximum of the v_{as} band of water (3705 cm⁻¹) in the 293-K spectrum of the CCl₄-containing solution, calculated as

Table 1. Equilibrium constant of GeCl₄ hydrolysis and molar extinction coefficient in the maximum of the v(OH) band of Ge(OH)Cl₃ at 293 K

$\begin{array}{c} C_{\rm H_{2}O} \times 10^{3},\\ \rm mol/l \end{array}$	$\begin{array}{c} C_{\mathrm{GeCl}_4} \times 10^2,\\ \mathrm{mol/l} \end{array}$	$K_C \times 10^3$	ϵ_v , l/(mol cm)
4.24	4.07	1.71	75.3
3.32	8.83	1.77	74.7
2.44	16.04	1.75	75.1
1.4–10	874.3*	1.64	74.6

* GeCl₄ concentration of 8.743 mol/l corresponds to pure germanium tetrachloride. described in [5]; and *l* is the thickness of the absorbing layer (cm).

The equilibrium of reaction (1) in high-purity germanium tetrachloride was studied over a wide range of water concentrations by measuring the intensities of the $\delta(H_2O)$ band at 1600 cm⁻¹ and the v(OH) band of Ge(OH)Cl₃ at 3603 cm⁻¹. To this end, a certain amount of tritiated water was dissolved, with vigorous stirring, without vaporization, in GeCl₄ in a thermostated reactor equipped with a flow cell. Only under such conditions could we determine the equilibrium amounts of monomeric water and GeCl₄ hydrolysis products (Ge(OH)Cl₃ and HCl). The completeness of water dissolution in GeCl₄ was checked by repeatedly recording the spectrum of the solution from 1100 to 4000 cm⁻¹ and also by a radiotracer technique [7]. From the maximum absorbances on the $\delta(H_2O)$ band at 1600 cm⁻¹ and the v(OH) band of Ge(OH)Cl₃ at 3603 cm⁻¹ in the spectrum of the solution and the maximum values of ε_v on these bands, evaluated as described in [7], we calculated the equilibrium reactant and product concentrations and the equilibrium constant of reaction (1) in high-purity germanium tetrachloride (Table 1).

We obtained the following results:

(1) At water concentrations from 10^{-3} to 10^{-2} mol/l, the equilibrium constant of reaction (1) varies very little, indicating that the assumption as to the mechanism of GeCl₄ hydrolysis at low water concentrations is correct. The same is evidenced by the fact that, at water concentrations below 10^{-2} mol/l, the molar extinction coefficients in the maximum of the v(OH) band of Ge(OH)Cl₃ calculated from the data on hydrolysis in CCl₄ and high-purity GeCl₄ (using the equilibrium constant of reaction (1) in CCl₄, $K_C = 1.74 \times 10^{-3}$) coincide (Table 1).

(2) Increasing the water concentration to above 10^{-2} mol/l increases the equilibrium constant of reaction (1), pointing to further replacement of chlorine according to the scheme

$$\operatorname{GeCl}_4 + n\operatorname{H}_2\operatorname{O} \Longrightarrow \operatorname{Ge}(\operatorname{OH})_n\operatorname{Cl}_{4-n} + n\operatorname{HCl},$$
 (6)

where n = 2 or 3. The same is evidenced by the appearance of a broad absorption band in the range 3000–3600 cm⁻¹.

(3) The equilibrium constant of reaction (1) is independent of the germanium tetrachloride concentration in solution up to extrapure GeCl_4 , in full accordance with the ideality of the GeCl_4 -CCl₄ system.

CHEMICAL EQUILIBRIUM IN ARSENIC TRICHLORIDE HYDROLYSIS

The equilibrium of reaction (2) was studied at water concentrations from 10^{-3} to 6×10^{-2} mol/l, using the same procedure as in the case of germanium tetrachlo-

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ride. The equilibrium reactant and product concentrations in reaction (2) were evaluated from the intensity of the $\delta(H_2O)$ band (1600 cm⁻¹) in the spectrum of the solution, using the maximum ε_v on this band determined as described in [7]. The results thus obtained are summarized in Table 2.

It can be seen from Table 2 that, at water concentrations in AsCl₃ below 3×10^{-2} mol/l, the equilibrium constant of hydrolysis varies little. This lends support to the assumption that, at low water concentrations, only the first stage of hydrolysis occurs. Raising the water concentration to above 3×10^{-2} mol/l increases the equilibrium constant of reaction (2), pointing to further replacement of chlorine according to the scheme

$$AsCl_3 + nH_2O \Longrightarrow As(OH)_nCl_{3-n} + nHCl,$$
 (7)

where n = 2 or 3.

The effect of $AsCl_3$ concentration on the equilibrium constant of reaction (2) was studied using CCl_4 by the same procedure as in the H₂O–GeCl₄–CCl₄ system.

A certain amount of high-purity AsCl₃, containing $<10^{-4}$ mol/l H₂O, was added to appropriate amounts of CCl₄ and water in a thermostated reactor. The IR transmission spectrum of the solution was recorded at 293 K from 3200 to 4000 cm⁻¹ before and after the introduction of arsenic trichloride (Fig. 2). As a result of hydrolysis, the intensity of the v_{as} band of water (3705 cm⁻¹) decreased, and the v(OH) band of As(OH)Cl₂ emerged at 3562 cm⁻¹.

In the spectra of CCl_4 -containing solutions, the frequency of the v(OH) band of As(OH)Cl₂ is substantially higher than the 3525 cm⁻¹ in the spectrum of high-purity AsCl₃, pointing to a weaker interaction of the OH group of As(OH)Cl₂ with CCl₄ molecules. Indeed, the energy of this interaction in the CCl₄-containing solution, evaluated by the Sokolov equation [8], is 2.76 kJ/mol, against 5.44 kJ/mol in high-purity AsCl₃. Moreover, at AsCl₃ concentrations above 0.1 mol/l, the v_{as} band of water is notably shifted to lower frequencies owing to the increased polarity of the medium.

The decrease in v_{as} frequency is accompanied by an increase in the molar extinction coefficient $\varepsilon_{v_{as}}$ of water. In view of this, at the equilibrium reactant and product concentrations in reaction (2), we refined the $\varepsilon_{v_{as}}$ of water using the experimentally determined dependence of $\varepsilon_{v_{as}}$ on the v_{as} frequency in the spectrum of the solution [7].

The equilibrium constants of arsenic trichloride hydrolysis in CCl_4 at low water concentrations are listed in Table 3. The equilibrium constant of reaction (2) var-



Fig. 2. IR transmission spectra of (1) H_2O and (2) $H_2O + AsCl_3$ solutions in CCl₄; 2.6 × 10⁻³ mol/l H_2O , 5.5 × 10⁻² mol/l AsCl₃, 10-cm absorbing layer.

ies little up to $\simeq 10^{-2}$ mol/l AsCl₃ and decreases at higher AsCl₃ concentrations, from 4.2×10^{-3} at low concentrations to 1.8×10^{-4} in pure arsenic trichloride.

CONCENTRATION DEPENDENCES OF THE EQUILIBRIUM CONSTANTS OF GeCl₄ AND AsCl₃ HYDROLYSIS IN CCl₄

Our results show that, at low water concentrations in the H_2O –GeCl₄–CCl₄ system, the equilibrium constant

Table 2. Equilibrium constant of AsCl₃ hydrolysis at 293 K

$C_{\rm H_2O} \times 10^3$, mol/l	$K_C \times 10^4$		
3.20	1.75		
7.32	1.64		
11.5	1.81	$\overline{K}_C = 1.8 \times 10^{-4}$	
15.6	1.72		
25.7	2.05	,	
35.9	3.68		
46.4	3.92		
56.6	4.25		



Fig. 3. Log–log plots of the distribution ratio vs. degree of distillation for dilute (1) germanium tetrachloride and (2) arsenic trichloride solutions in carbon tetrachloride.

of reaction (1) remains constant over a wide range of $GeCl_4$ concentrations.

At the same time, in the $H_2O-AsCl_3-CCl_4$ system the equilibrium constant of reaction (2) depends strongly on $AsCl_3$ concentration.

It seems likely that this difference can be understood in terms of the intermolecular interactions in the $GeCl_4$ - CCl_4 and $AsCl_3$ - CCl_4 systems.

As is well known, intermolecular interactions can be characterized by the activity coefficient γ . In this context, it is of interest to correlate the activity coefficients of GeCl₄ and AsCl₃ in the binary systems in question with the equilibrium constant of hydrolysis.

One way of determining the activity coefficient of a component of the liquid phase is by investigating the liquid–vapor equilibrium [9]. We studied the liquid–vapor equilibria for dilute $GeCl_4$ and $AsCl_3$ solutions in

 CCl_4 using simple equilibrium distillation [10]. The variation in vapor composition was followed by a radiotracer (⁷¹Ge and ⁷⁶As) technique [11].

As shown earlier [10], equilibrium distillation of a dilute solution can be described by the equation

$$\log \overline{K} = (m-1)\log \overline{\varphi} + \log m. \tag{8}$$

Here, $m = \alpha$ for volatile impurities and $m = 1/\alpha$ for nonvolatile impurities, α is the separation coefficient, $\overline{\phi} = G_i/G_0$ is the degree of distillation (where G_i is the amount of the solution in the still during distillation, and G_0 is the initial amount of the solution), and $\overline{K} = y_i/x_0$ is the distribution ratio (where y_i is the impurity content of the vapor phase during distillation, and x_0 is the initial impurity content of the solution). Since the volatility of GeCl₄ and AsCl₃ is low compared to CCl₄, we take $m = 1/\alpha$ in Eq. (8).

The experimental data on equilibrium distillation are presented in Fig. 3.

The linear relationship between $\log \overline{K}$ and $\log \overline{\varphi}$ indicates that, in dilute GeCl₄ and AsCl₃ solutions in CCl₄, Henry's law ($\alpha = \text{const}$) is obeyed, and the solute is present in only one chemical form.

Using the results on equilibrium distillation and Eq. (8), we calculated the separation coefficients (α_{exp}) and activity coefficients of solutes (γ_s) at low GeCl₄ and AsCl₃ concentrations (Table 4).

It follows from the data in Table 4 that the GeCl₄– CCl₄ system behaves ideally, while the AsCl₃–CCl₄ system exhibits a significant positive deviation from ideality. At low AsCl₃ concentrations, the value of γ_{AsCl_3} agrees well with the data on the liquid–vapor equilibrium in the AsCl₃–CCl₄ system at high concentrations [12]. According to earlier results [12], the AsCl₃–CCl₄ system can be classed with regular solutions and described by the Van Laar equation with two

Table 3. Equilibrium constant of AsCl₃ hydrolysis at 293 K as a function of AsCl₃ concentration in CCl₄

$C_{\text{AsCl}_3} \times 10^3$, mol/l	5.5	7.7	11	22	55	442	1410	4180	11930*
$K_C \times 10^3$	4.32	4.10	4.13	3.50	3.12	2.63	1.62	0.75	0.18

* Concentration of 11.93 mol/l corresponds to pure arsenic trichloride.

virial coefficients A and B [8],

$$\log \gamma_{1} = \frac{A}{\left(1 + \frac{Ax_{1}}{B(1 - x_{1})}\right)^{2}},$$
(9)

$$\log \gamma_2 = \frac{B}{\left(1 + \frac{B(1 - x_1)}{Ax_1}\right)^2},$$
 (10)

where $A = \log \gamma_1$ for $x_1 \longrightarrow 0$, and $B = \log \gamma_2$ for $1 - x_1 \longrightarrow 0$.

In the AsCl₃–CCl₄ system, A = B.

Therefore, we have $A = B = \log \gamma_{AsCl_3}$ $(x \longrightarrow 0) = \log 1.85 = 0.267$. The variation of γ_{AsCl_3} with AsCl₃ concentration at x < 0.1 can be calculated by the formula

$$\log \gamma_{AsCl_{3}} = \frac{\log \gamma_{AsCl_{3}}(x \longrightarrow 0)}{1 + \left(\frac{x_{AsCl_{3}}}{1 - x_{AsCl_{3}}}\right)^{2}} = \frac{0.267}{\left(1 + \frac{x_{AsCl_{3}}}{1 - x_{AsCl_{3}}}\right)^{2}}.$$
(11)

Figure 4 shows the concentration dependences of K_C and γ_{AsCl_3} . Because of the low water concentration, the impurities present in the water have no significant effect on γ_{AsCl_3} or γ_{CCl_4} . It can be seen that $\log K_C$ and $\log C_{AsCl_3}$ vary with $\log C_{AsCl_3}$ in a similar way. Accordingly, $\log K_C$ is a linear function of $\log \gamma_{AsCl_3}$ (Fig. 5) and can be represented in the form

$$\log K_C = \log K_{C_{(AsCl_3)}} + 5.2 \log \gamma_{AsCl_3}.$$
 (12)

In the GeCl₄–CCl₄–H₂O system, $\gamma_{GeCl_4} = 1$ and

$$\log K_C = \log K_{C_{\text{GeCL}}}.$$
 (13)

Thus, the concentration effect on the equilibrium constant of the reaction $AsCl_3 + H_2O \implies As(OH)Cl_2 + HCl$ in CCl_4 is associated with the dependence of the activity coefficient γ_{AsCl_3} in the $AsCl_3$ – CCl_4 system on the $AsCl_3$ concentration.

EQUILIBRIA IN GERMANIUM TETRACHLORIDE AND ARSENIC TRICHLORIDE HYDROLYSIS AT DIFFERENT TEMPERATURES

The effect of temperature on the equilibrium of reactions (1) and (2) in CCl_4 was studied using solutions containing $(2-6) \times 10^{-3} \text{ mol/l H}_2\text{O}$, $3 \times 10^{-3} \text{ to } 5 \times 10^{-3} \text{ mol/l H}_2\text{O}$, $3 \times 10^{-3} \text{ to } 5 \times 10^{-3} \text{ mol/l H}_2\text{O}$, $3 \times 10^{-3} \text{ to } 5 \times 10^{-3} \text{ mol/l H}_2\text{O}$.

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Fig. 4. Log–log plots of the (1) activity coefficient and (2) equilibrium constant of reaction (2) vs. $AsCl_3$ concentration in CCl_4 .



Fig. 5. Log–log plot of the equilibrium constant of AsCl₃ hydrolysis vs. AsCl₃ activity coefficient.

 10^{-1} mol/l GeCl₄, and $(2-9) \times 10^{-3}$ AsCl₃. The spectra of the solutions were recorded continuously between 3200 and 4000 cm⁻¹ until fully reproducible results were obtained, indicating that the equilibrium of reactions (1) and (2) was reached.

Table 4. Separation coefficients and activity coefficients for dilute GeCl_4 and AsCl_3 solutions in CCl_4 (pressure, 10⁵ Pa; boiling point, 76.5°C; equilibrium solute concentrations from 10^{-3} to 10^{-4} wt %)

Solute	Boiling point, °C	α_{ideal}	α_{exp}	$\gamma_{ m s}$
GeCl ₄	83.1	1.20	1.20	1.00
AsCl ₃	130.1	5.60	3.03	1.85



Fig. 6. IR transmission spectra of an $H_2O + GeCl_4$ solution in CCl_4 at (1) 283, (2) 303, and (3) 333 K; 10-cm absorbing layer.

Figures 6 and 7 show the spectra of $H_2O + GeCl_4$ and $H_2O + AsCl_3$ solutions in CCl_4 at different temperatures. With increasing temperature, the intensity of the v_{as} band of water (3705 cm⁻¹) decreases, while the intensities of the v(OH) bands of Ge(OH)Cl_3 (3603 cm⁻¹) and As(OH)Cl_2 (3562 cm⁻¹) decrease. These results indicate that raising the temperature drives reactions (1) and (2) to the right. From the maximum absorbance on the v_{as} band of water in the spectra of the solutions studied and the maximum molar extinction coefficient on this band, we evaluated, by Eq. (3), the equilibrium reactant and product concentrations and the equilibrium constants of reactions (1) and (2) at different temperatures (Table 5).

The equilibrium constants of reactions (1) and (2) show Arrhenius behavior (Fig. 8), with best fit equations

$$\log K_C = 1.039 - 1113/T, \tag{14}$$

$$\log K_C = 0.928 - 974/T. \tag{15}$$

The temperature-dependent equilibrium constants of reactions (1) and (2) were used to evaluate the mean standard heat effect of reaction ΔH^0 , standard Gibbs energy change ΔG^0 , and standard entropy change ΔS^0 (Table 5). In the temperature range studied, the ΔH^0 values of reactions (1) and (2) vary little. At the same time,



Fig. 7. IR transmission spectra of an $H_2O + AsCl_3$ solution in CCl₄ at (1) 283, (2) 303, and (3) 333 K; 10-cm absorbing layer.

with increasing temperature, ΔG^0 decreases and ΔS^0 increases. These results demonstrate that reactions (1) and (2) are endothermic.

Using the mean standard heat effects of reactions (1) and (2) and the standard heats of formation of the compounds involved [13], we estimated the standard heats of



Fig. 8. Arrhenius plots of K_C for reactions (1) and (2).

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<i>Т</i> , К	$K_C \times 10^{-3}$	ΔH^0 , kJ/mol	ΔG^0 , kJ/mol	$\Delta S^{0},$ kJ/(mol K)		
$GeCl_4 + H_2O = Ge(OH)Cl_3 + HCl$						
283.15	1.30	20.75	15.64	18.05		
293.15	1.77	20.75	15.45	18.08		
298.15	2.05	20.75	15.34	18.14		
303.15	2.36	20.75	15.25	18.16		
313.15	3.09	20.75	15.05	18.20		
323.15	3.97	20.75	14.86	18.23		
333.15	5.04	20.75	14.65	18.37		
$AsCl_3 + H_2O = As(OH)Cl_3 + HCl$						
283.15	3.06	18.32	13.63	16.56		
293.15	4.02	18.32	13.44	16.65		
298.15	4.57	18.32	13.35	16.67		
303.15	5.18	18.32	13.26	16.69		
313.15	6.57	18.32	13.08	16.73		
323.15	8.22	18.32	12.90	16.77		
328.15	9.15	18.32	12.81	16.79		
333.15	10.15	18.32	12.70	16.84		

Table 5. Equilibrium constants and thermodynamic characteristics of $GeCl_4$ and $AsCl_3$ hydrolysis in CCl_4

formation of Ge(OH)Cl₃ and As(OH)Cl₂ in CCl₄-containing solutions: $\Delta_{\rm f} H^0(298 \text{ K}, \text{Ge}(OH)Cl_3) = -663.9 \text{ kJ/mol}$ and $\Delta_{\rm f} H^0(298 \text{ K}, \text{As}(OH)Cl_2) = -402.8 \text{ kJ/mol}$.

CONCLUSION

The equilibria in GeCl₄ and AsCl₃ hydrolysis in CCl₄ were studied at low water concentrations. The results demonstrate that the equilibrium constant of the reaction GeCl₄ + H₂O \implies Ge(OH)Cl₃ + HCl is independent of the GeCl₄ concentration in solution up to extrapure GeCl₄, because the GeCl₄–CCl₄ system behaves ideally ($\gamma_{GeCl_4} = 1$).

The equilibrium constant of the reaction AsCl₃ + $H_2O \implies As(OH)Cl_2$ depends on the AsCl₃ concentration in CCl₄, which is associated with the variation in γ_{AsCl_3} : $\log K_C = \log K_{C(AsCl_3)} + 5.2 \log \gamma_{AsCl_3}$.

We calculated the equilibrium constants and thermodynamic characteristics of GeCl_4 and AsCl_3 hydrolysis in CCl_4 in the range 283–333 K and the standard heats of formation of $\text{Ge}(\text{OH})\text{Cl}_3$ and $\text{As}(\text{OH})\text{Cl}_2$.

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